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AN APPLICATION OF HIRSCHFELDER-SILBEY PERTURBATION THEORY
TO THE H_2^+ ION: A CRITICISM OF AND CORRECTION TO WIS-TCI-180* (N66 37904)

by

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* This research was supported by the National Aeronautics
and Space Administration Grant NsG-275-62.

Herein we report an error occurring in WIS-TCI-180¹ by R. B. Hake, Robert J. Silbey, and Joseph O. Hirschfelder in which the Hirschfelder-Silbey perturbation technique is applied through first order to the lowest gerade and ungerade states of the H_2^+ ion. The calculations have been performed once again with the following ideas included. Results are listed at the end of this report and indicate that the disparity in agreement between our values of $\mathcal{E}_g(\cdot)$ and $\mathcal{E}_u(\cdot)$ with the corresponding "exact" values of Peek² is roughly the same for the gerade as for the ungerade state. Previously it was reported that the ungerade energy was in very good agreement while the corresponding gerade energy was relatively poor. It might now be said that agreement of $\mathcal{E}_g(\cdot)$ and $\mathcal{E}_u(\cdot)$ with the values of Peek is "fair" for both states.

The essential idea to be pointed out here is that once the basis functions on nucleus a have been chosen the corresponding states on nucleus b are uniquely specified by the action of the reflection operator σ . (The notation is that of WIS-TCI-180 and WIS-TCI-168A³.) In WIS-TCI-180 the phase factor $(-1)^l$ was inadvertently introduced by defining the basis functions on nucleus b -- once the basis functions on nucleus a had already been chosen -- in terms of the wrong polar angle. As shown in fig. 1, an orbital centered on nucleus a and specified by the quantum numbers η and

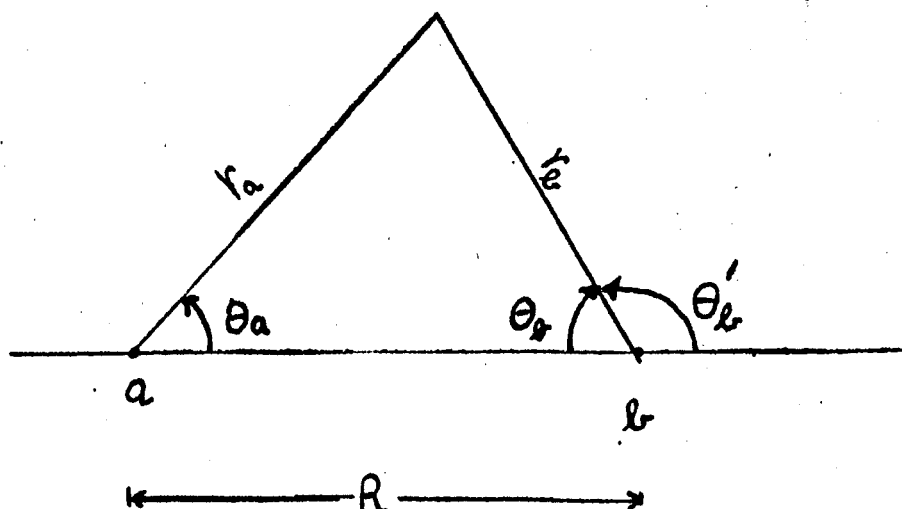


Fig. 1

l may be written in terms of the Löwdin orbitals and Legendre polynomials as

$$\psi_{nl}(a) = R_{nl}(r_a) P_l(\cos \theta_a). \quad (1)$$

The corresponding orbital centered on nucleus b , that is, $\psi_{nl}(b) = \sigma \psi_{nl}(a)$ should be written as

$$\psi_{nl}(b) = R_{nl}(r_b) P_l(\cos \theta_b) \quad (2)$$

with θ_b defined, as in fig. 1, in the clockwise sense. In terms of the variables used in WIS-TCI-180, we find

$$\cos \theta_b = \frac{(1 - \xi \eta)}{(\xi - \eta)} \quad (3)$$

where

$$\begin{aligned} \xi &= \frac{r_a + r_b}{R} \\ \eta &= \frac{r_a - r_b}{R} \end{aligned} \quad (4)$$

As a matter of fact, however, with the orbitals on Q defined as in (1), the orbitals centered on nucleus b were defined as

$$\psi_{nl}(b) = R_{nl}(r_b) P_l(\cos \theta'_b) \quad (5)$$

where

$$\cos \theta'_b = \frac{(\xi r - 1)}{(\xi - r)} \quad (6)$$

Clearly we have that

$$\cos \theta'_b = -\cos \theta_b \quad (7)$$

which consequently leads to

$$P_l(\cos \theta'_b) = (-1)^l P_l(\cos \theta_b) \quad (8)$$

whence the erroneous phase factor.

Indeed, such an error in defining the phase will have a serious effect upon the matrix elements to be computed for the calculation. Consider, for example, the overlap integral $\langle \psi_{21}(a) | \psi_{21}(b) \rangle$. The "angular dependences" of the functions $\psi_{21}(a)$ and $\psi_{21}(b)$ are shown in figs. 2a and 2b respectively. Now, since the functions are normalized, in the limit that the molecular bond length R approaches zero, the overlap integral should approach minus one. One may check from formula 3 of the appendix of WIS-TCI-180 that, because of the erroneous

phase factor, the overlap integral $\langle \psi_{a1}(\omega) / \psi_{a1}(b) \rangle$ approaches plus one in the limit that the bond length reaches zero. Similar inconsistencies were discovered in other formulas and were traced to the phase factor $(-1)^l$.

The orbitals centered on nucleus b and defined correctly as in (2) were inserted into the Program H2PLUS constructed by R. Hake. It is a very beautiful program, and extremely easy to correct. In fact to insure the correct phase associated with the orbitals centered on b , only one card in the entire program need be changed. In the subroutine ALL the statement

$$121 \quad IS = IS2 - IU2 + JU2$$

should read

$$121 \quad IS = IS2 - IU2$$

The values of the newly computed matrix elements were found to agree with those calculated via another program being constructed to attack the H_2^+ problem via Hirschfelder-Silbey perturbation theory. Much of the work on the latter program was done by Mrs. Wanda Giese.

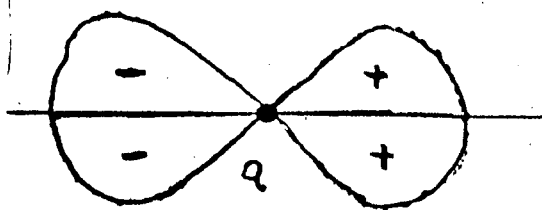


Fig. 2a

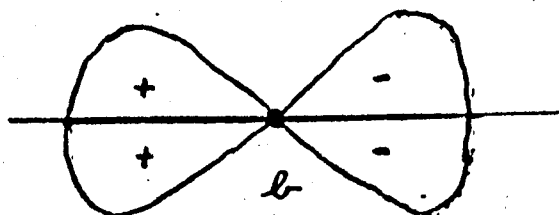


Fig. 2b

In rerunning the H2PLUS Program another mistake was discovered in the main program. The card

$$B14 = B14 + A5 * B6$$

should in fact read

$$B14 = B14 + A2 * (B15 + B6).$$

This card is involved in the evaluation of the quantity $\langle q^{(n)} | V_a | b^{(n)} \rangle$.

The change reflects the inequivalence of the matrix elements $\langle q^{(n)} | V_a | \psi_{n,l}^{(a)} \rangle$ and $\langle b^{(n)} | V_a | \psi_{n,l}^{(a)} \rangle$ which was assumed by use of the original statement.

To conclude, we note that WIS-TCI-180 would read correctly if, on p. 10

$$\cos \theta_{lr} = \frac{(\xi n - 1)}{(\xi - n)}$$

would be replaced by

$$\cos \theta_{lr} = \frac{(1 - \xi n)}{(\xi - n)}$$

and in formulas No. 3 and No. 9 in the appendix the quantity $(-1)^{s'+q'+u'}$ were $(-1)^{s'+u'}$.

In formula No. 9 there is apparently a printing error which did not carry over into the computations: $\beta(l+p-q-s+u+l'+p'-q'+u'+1)$ should, in fact, read $\beta(l+p-q-s+u+l'+p'-q'-s'+u'+1)$.

TABLE 1: Corrected Energy Values for H_2^+ for $R = 2a.u.$

No. of Basis Functions	$\epsilon_g^{(2)}$	$\epsilon_g^{(3)}$	$\epsilon_g^{(1)} + 1/R$	$\epsilon_u^{(2)}$	$\epsilon_u^{(3)}$	$\epsilon_u^{(1)} + 1/R$
1	-0.0394198	0.0040972	-0.5883357	0.0431480	-0.0028658	-0.1214920
2	-0.0447604	0.0047930	-0.5927570	0.0591891	-0.0013156	-0.1055082
3	-0.0489759	0.0170607	-0.5840042	0.0321237	-0.0008984	-0.1309428
4	-0.0530448	0.0143872	-0.5897072	0.0137844	+0.0000410	-0.1472716
5	-0.0537877	0.0137599	-0.5913862	0.0126168	-0.0018098	-0.1498745
6	-0.0541226	0.0120797	-0.5932908	0.0123791	-0.0022611	-0.1504436
7	-0.0541270	0.0120578	-0.5933183	0.0123953	-0.0022787	-0.1504407
8	-0.0542692	0.0118774	-0.5932246	0.0089067	-0.0004466	-0.1524764
9	-0.0543271	0.0115324	-0.5938201	0.0070787	-0.0005195	-0.1543222
10	-0.0543849	0.0114354	-0.5940061	0.0068882	-0.0005666	-0.1545442

All energy values are in atomic units.

$$\epsilon^{(0)} = -0.5$$

Peek's values:

$$\epsilon_g^{(1)} + 1/R = -0.6026342$$

$$\epsilon_g^{(1)} = -0.5537715$$

$$\epsilon_u^{(1)} + 1/R = -0.1675344$$

$$\epsilon_u^{(1)} = -0.1608540$$

$$\epsilon_g^{(0)} + 1/R = -0.5537715$$

$$\epsilon_u^{(0)} + 1/R = -0.1608540$$

REFERENCES

1. R. B. Hake, Robert J. Silbey, and Joseph O. Hirschfelder, An Application of Hirschfelder-Silbey Perturbation Theory to the H_2^+ ion, WIS-TCI-180.
2. J. M. Peek, Sandia Corporation Report SC-RR-65-77 (1966).
3. J. O. Hirschfelder and R. J. Silbey, A New Type of Molecular Perturbation Theory, WIS-TCI-168A.